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Theory of electronic states and formation energies of defect complexes, interstitial defects and crystal growth in semiconductors. Period covering Aug. 87-Oct. 88.

During this period, three main areas of our research were focused on. The first is the prediction of deep levels and equilibrium concentrations of defects in semiconductors, second is the mathematical development of an ab-initio tight binding theory for quantum molecular dynamics calculations, and finally the third area was a pseudo-atomic-orbital band theory applied to electron energy loss near edge structures.

The project on defects and their equilibrium concentration has been an area of active research for the last couple of years. We have now successfully completed calculations on GaAs, ZnSe, ZnTe and GaP. The purpose of this work was to determine the dominant native defects in these materials, and to investigate trends. We have investigated [1] [2] several factors which influence which defect is the dominant defect in these materials. These factors are stoichiometry, temperature, chemical potential and the presence of extrinsic impurities.

The intrinsic defects considered are the anion and cation antisites $A_C$ and $C_A$ (an anion antisite is when an anion atom occupies a site normally occupied by a cation atom), the anion and cation tetrahedral-site interstitial defects $A(T_A)$, $A(T_C)$, $(T_A)$ and $C(T_C)$ at the two non-equivalent tetrahedral sites $T_A$ (surrounded anion) and $T_C$ (Surrounded by cations). The extrinsic impurities (denoted X) are the anion- and cation- site substitional defects $X_A$ and $X_C$, and the two interestitial-site defects $X(T_A)$ and $X(T_C)$.

Defects play a fundamental role in the electronic properties of materials. Fabrication of materials of desired quality requires extensive knowledge of the probable concentration of defects. Unfortunately, a complete picture for defect formation is not yet available experimentally, and theoretical work has not, until recently, tackled this problem.

The relative abundance of point defects can in principle be predicted from equilibrium statistical mechanics once the defect formation energies are known. By writing defect reactions, the defect concentrations can be obtained from the energies of the defect reactions. The defect reactions are shown in Fig. 1. The notation $[A_C]$ means the concentration of $A_C$ defects (anion on a cation site).

In the last technical report, we discussed GaAs. So here we concentrate on ZnSe, ZnTe, and GaP.

We show the formation energies $E\mu(X)$ vs. chemical potential for ZnSe, ZnTe, and GaP in figures 2, 3, and 4 respectively. These formation energies are the results of self-consistent local density approximation electronic structure calculations. The formation energies are those appearing in the reactions in Fig. 1. The energies depend on the Fermi level of the material, since defects may form donors, acceptors, or deep levels. For instance, a donor impurity costs less energy to form in p-type material than n-type material because its electron can fall down across the semiconducting bandgap. Changes in slope of the curves appear at the location of deep levels in the band gap. As the Fermi level changes, the electron occupancy of the deep level changes causing the energy of the defect to change.

We show the relative defect concentrations in GaP as a function of relative stoichiometry in Fig. 5 for n- and p-type materials. The stoichiometry S is zero when the material is perfectly stoichiometric (the number of Ga atoms is

Figure 1. The defect reactions used to calculate the defect concentrations of intrinsic and extrinsic impurities. The top eight reactions are for intrinsic impurities and the bottom four are for extrinsic impurities. The reactions are on the left and a relationship between defect concentrations are on the right. This set of equations determines the defect concentrations in equilibrium. The energies $E_\alpha$ are determined by self-consistent electronic structure calculations.

INTRINSIC DEFECTS: $A_C$, $C_A$, $V_A$, $V_C$, $A_{T_A}$, $A_{T_C}$, $C_{T_A}$, $C_{T_C}$

| REACTION | EQUATION |
|---|---|
| $A_A + C_C \Longleftrightarrow A_C + C_A$ | $[A_C][C_A] = e^{-\beta(E_{A_C} + E_{C_A})}$ |
| $0 \Longleftrightarrow V_A + V_C$ | $[V_A][V_C] = e^{-\beta(E_{V_A} + E_{V_C})}$ |
| $A_A + V_C \Longleftrightarrow A_C + V_A$ | $[V_A][A_C] = [V_C]e^{-\beta(E_{A_C} + E_{V_A} - E_{V_C})}$ |
| $A_A \Longleftrightarrow V_A + A_{T_A}$ | $[V_A][A_{T_A}] = e^{-\beta(E_{V_A} + E_{A_{T_A}})}$ |
| $A_A \Longleftrightarrow V_A + A_{T_C}$ | $[V_A][A_{T_C}] = e^{-\beta(E_{V_A} + E_{A_{T_C}})}$ |
| $C_C \Longleftrightarrow V_C + C_{T_A}$ | $[V_C][C_{T_A}] = e^{-\beta(E_{V_C} + E_{C_{T_A}})}$ |
| $C_C \Longleftrightarrow V_C + C_{T_C}$ | $[V_C][C_{T_C}] = e^{-\beta(E_{V_C} + E_{C_{T_C}})}$ |

$$S = 2([A_C] - [C_A]) + ([V_C] - [V_A]) + ([A_{T_A}] + [A_{T_C}] - [C_{T_A}] - [C_{T_C}])$$
$$= (N_A - N_C)/N_L$$

EXTRINSIC DEFECTS: $X_A$, $X_C$, $X_{T_A}$, $X_{T_C}$

| | |
|---|---|
| $X_A \Longleftrightarrow X_{T_A} + V_A$ | $[X_{T_A}][V_A] = [X_A]e^{-\beta(E_{X_{T_A}} + E_{V_A} - E_{X_A})}$ |
| $X_A \Longleftrightarrow X_{T_C} + V_A$ | $[X_{T_C}][V_A] = [X_A]e^{-\beta(E_{X_{T_C}} + E_{V_A} - E_{X_A})}$ |
| $X_C \Longleftrightarrow X_{T_A} + V_C$ | $[X_{T_A}][V_C] = [X_C]e^{-\beta(E_{X_{T_A}} + E_{V_C} - E_{X_C})}$ |

$$S_X = [X_A] + [X_C] + [X_{T_A}] + [X_{T_C}]$$
$$= N_X/N_L$$

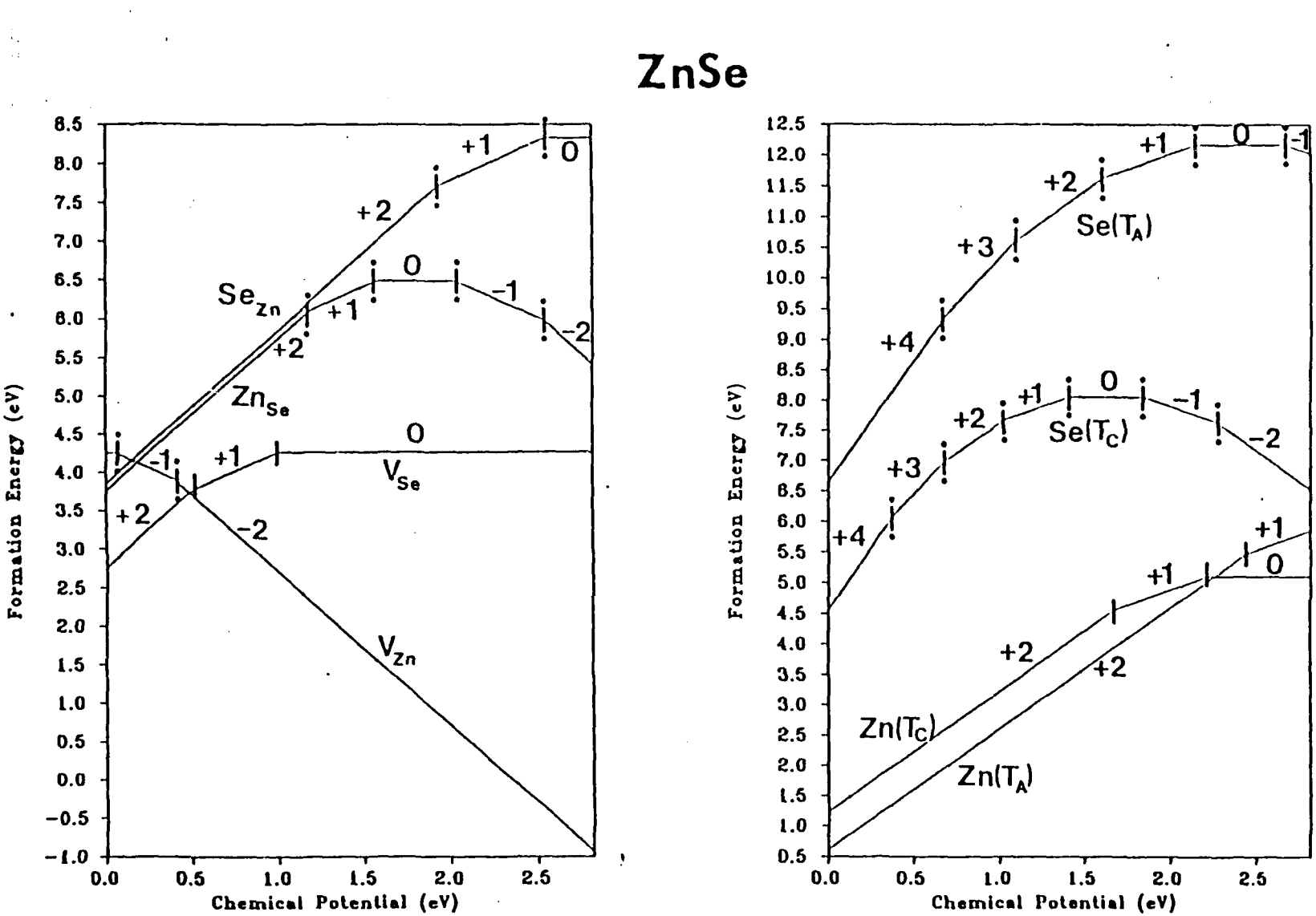



Figure 2. The formation energies of various intrinsic defects in ZnSe as a function of chemical potential. The chemical potential lies between the valence band edge (0.0eV) and the conduction edge. The breaks in slope of indivdual lines occur at deep levels for each of the impurities.

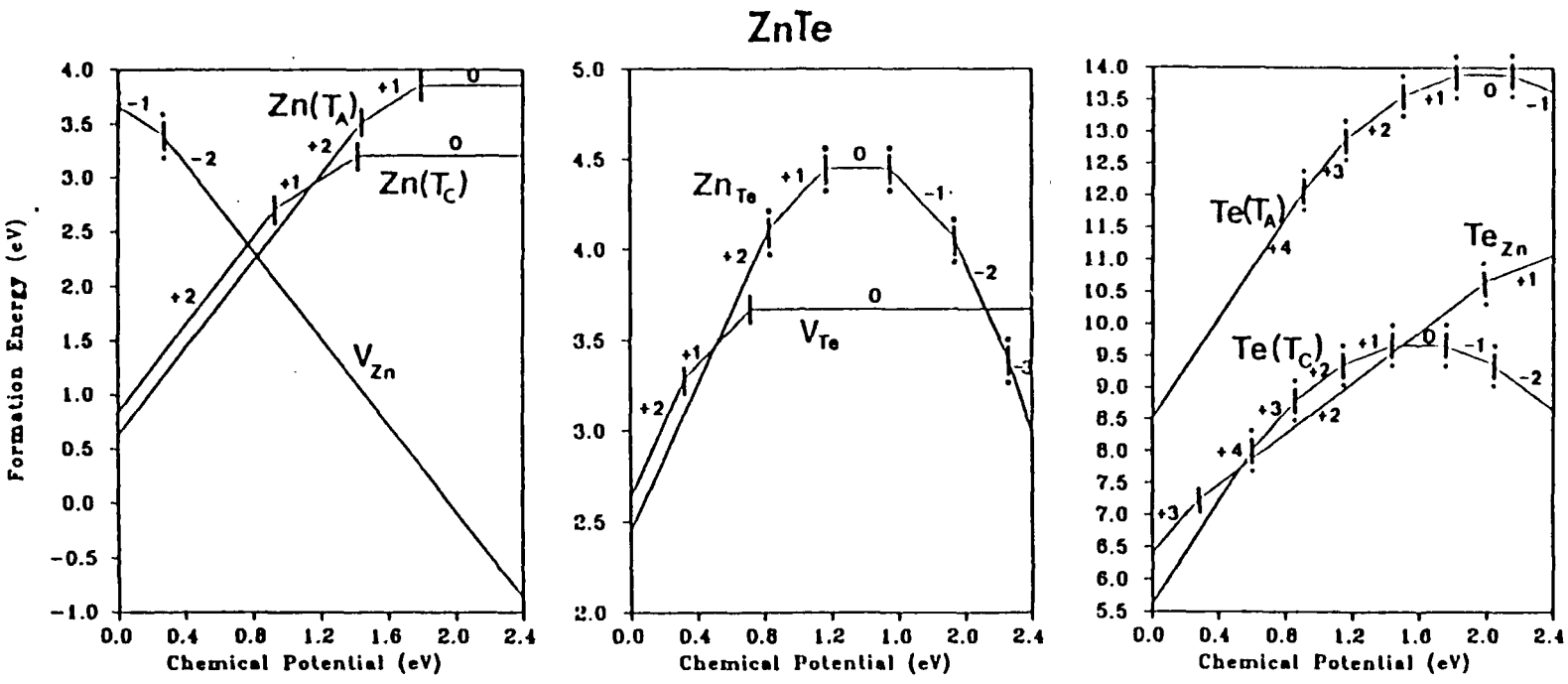



Figure 3. Same as figure 2, but for ZnTe.

Figure 4. Same as figure 2, but for GaP.

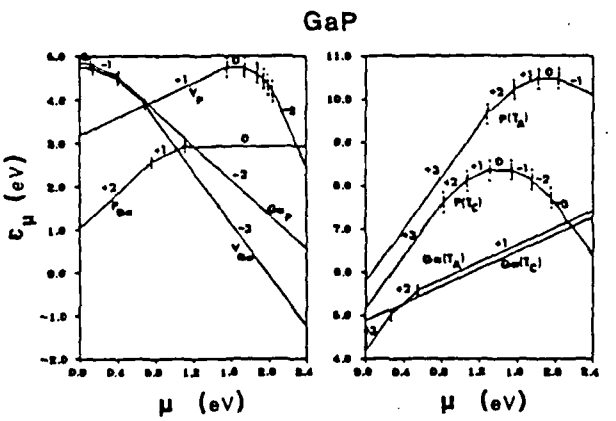
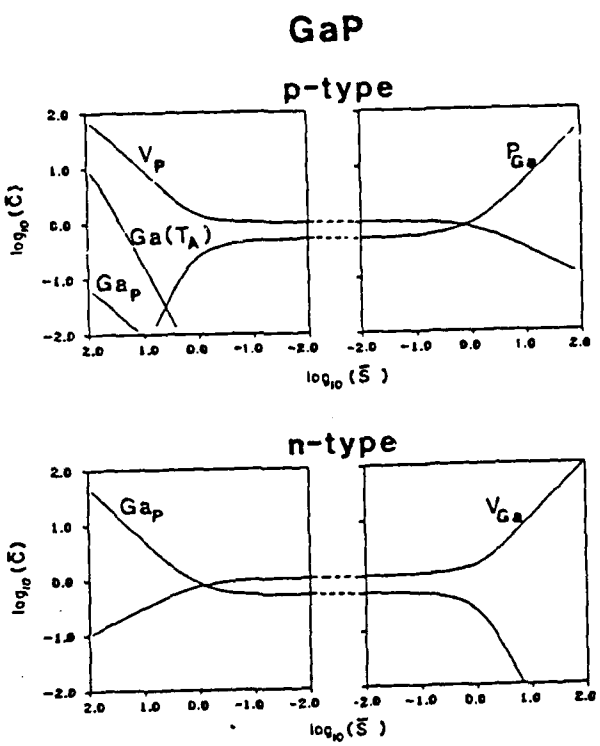


Figure 5. Native defect concentrations as a function of stoichiometry for p- and n-type GaP. The right panel is for positive stoichiometry S (excess P) and the left panel is for negative stoichiometry S (excess Ga). The center point between panels corresponds to perfect stoichiometry.



equal to the number of P atoms). We find that the dominant defect in either type is a vacancy, and the vacancy is at the P-site in n-type and at the Ga site in p-type. This unusual reversal occurs because the phosphous vacancy Vp is donor-like, while the Ga vacancy $V_{Ga}$ is acceptor-like. This dramatically illustrates the importance of the Fermi level in determining the dominant defect.

We show similar results for ZnSe, and ZnTe in Figs. 6 and 7 respectively. Interestingly, we find in p-type ZnTe that <u>interstitial</u> Zn ($Zn_{T_A}$) is the dominant defect. Interstitials in the III-V materials GaAs and GaP were not very abundant. Thus our results show that interstitials may play a much more important role in II-VI materials than in III-V materials. Our work has led to a new understanding of the energetics of interstitial defects [2].

This work has led to a Ph.D. thesis by Dr. Robert W. Jansen, which was defended in December 1987.

The second area of development of this project has been the mathematical formulation of an ab-initio multicenter tight-binding model for molecular dynamics simulations. The basic idea here is to combine Newton's laws of motion for the nuclei with the Schrodinger equation for the motion of the electrons, to describe dynamical processes in semiconductors such as diffusion, melting, or growth.

We have now completed most of the mathematical description of such a method and now move on to programming it in FORTRAN, and actually making it practical.

The final focus during this period has been on electron-energy-loss spectra, and its interpretation through the use of pseudo-atomic-orbital band theory.

At ASU, we have a strong effort in electron microscopy. One subset of work in this area is that of electron energy loss spectroscopy (EELS). The high

Figure 6. Same as figure 5, but for ZnSe.

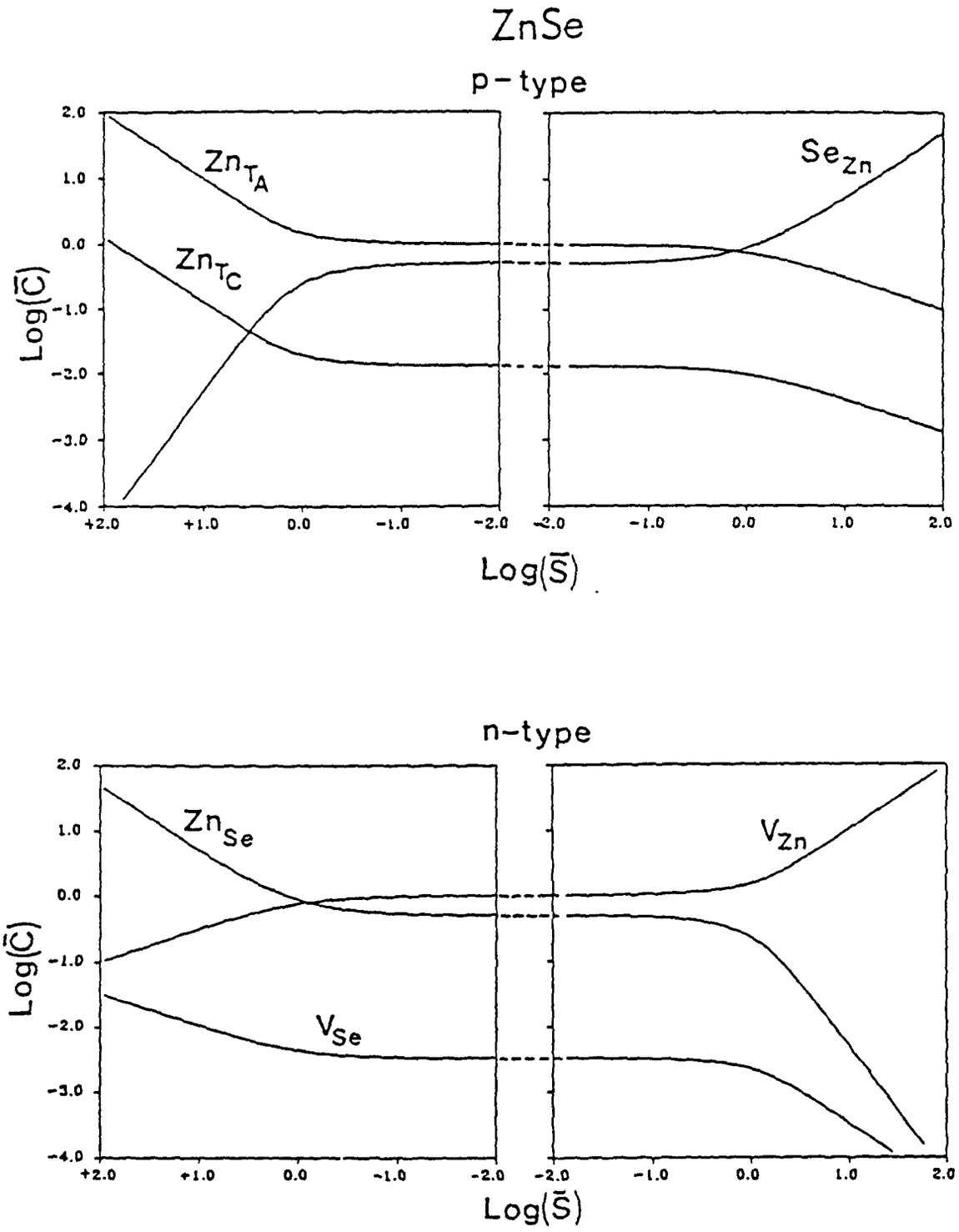
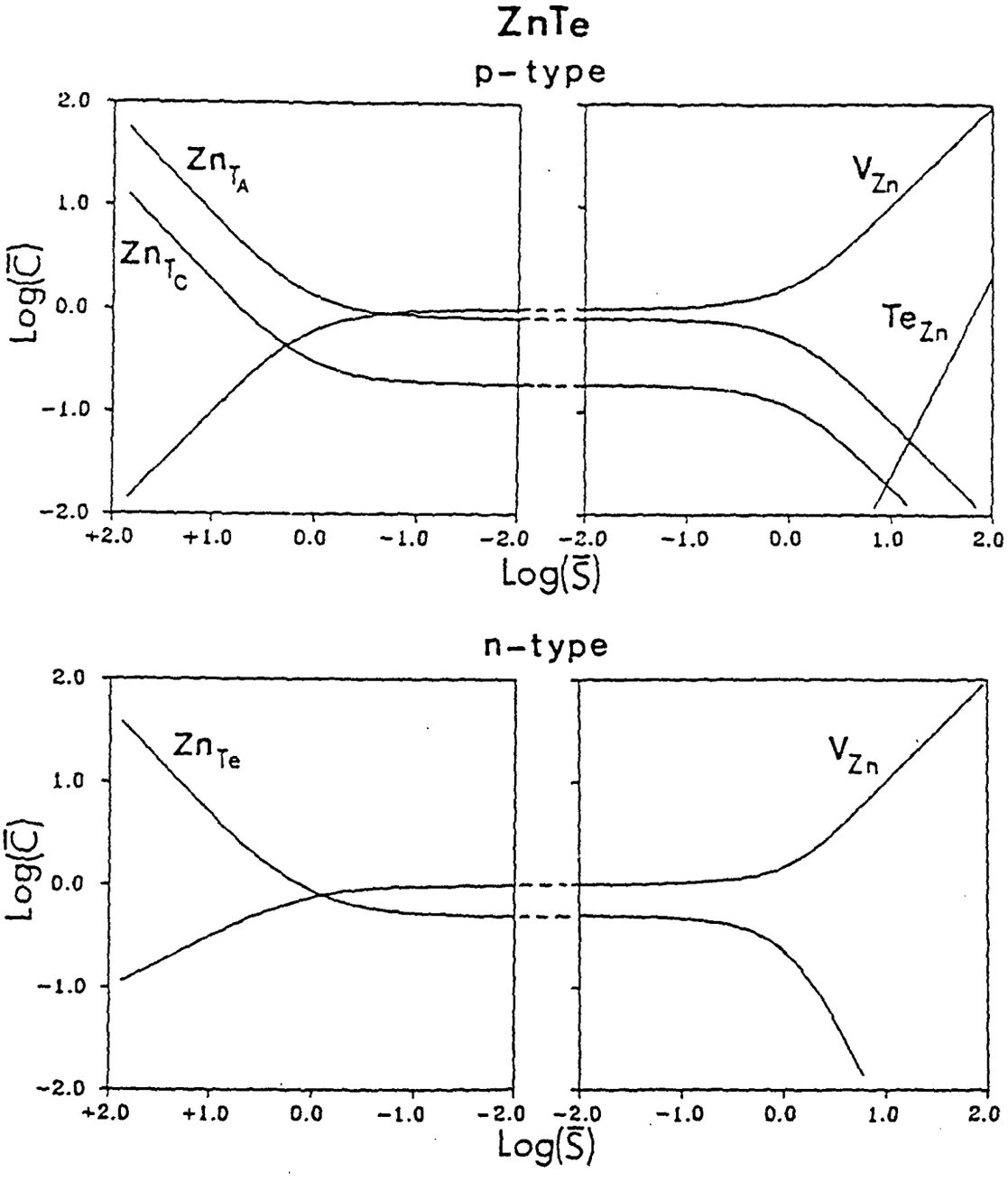


Figure 7. Same as figure 5, but for ZnTe.

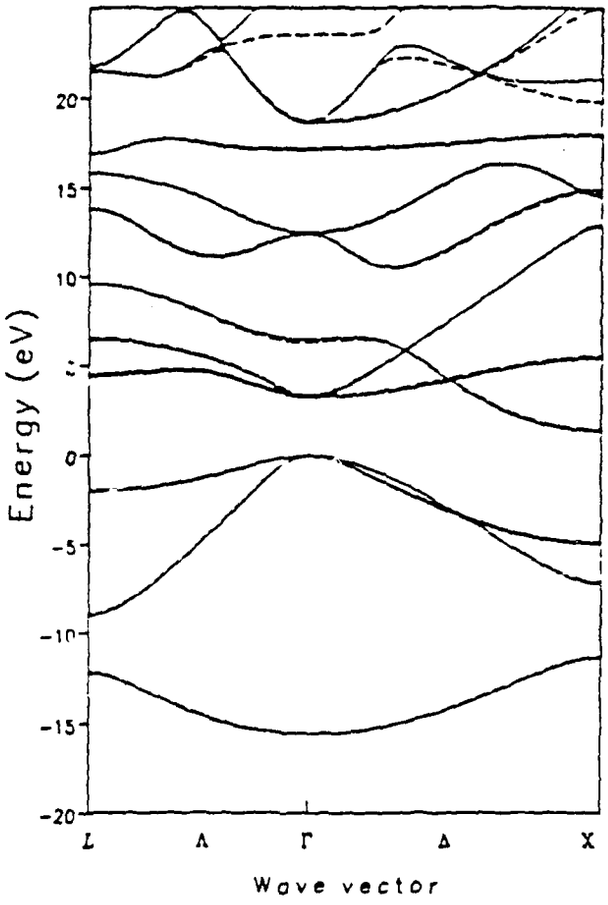


energy part of the spectrum is interpreted in terms of EXAFS like oscillations. The low energy part near edge structure (NES) is more difficult to interpret. We have used our first-principle tight-binding like electronic structure method [4] to calculate from first principles the near edge structure of Si, SiC, and $Be_2C$. We are able to explain the data very nicely in terms of this single electron picture. Some of these systems were previously thought to have very complicated many-body interactions in the NES. We find that such effects are unnecessary to understand the data. We were able to calculate spectra for these systems which are in closer agreement with experiment than with any other theoretical technique. The technique is very general and can be used to investigate a wide variety of materials.

We show an example of such a calculation in Fig. 8. This figure shows the band structure of $Be_2C$ and the near edge structure of the Be K-excitation. The excitations are to the conduction band states (states above 0.0 eV in Fig. 8a) from the Be core states (not shown). The NES is compared with experiment and is found to agree remarkably well over ~20eV. A combination of theory and experiment of NES may lead to new and useful techniques for materials science investigations concerning atomic environments and contamination in solids. This work is expected to lead to a Ph.D. thesis for Xudong Weng.

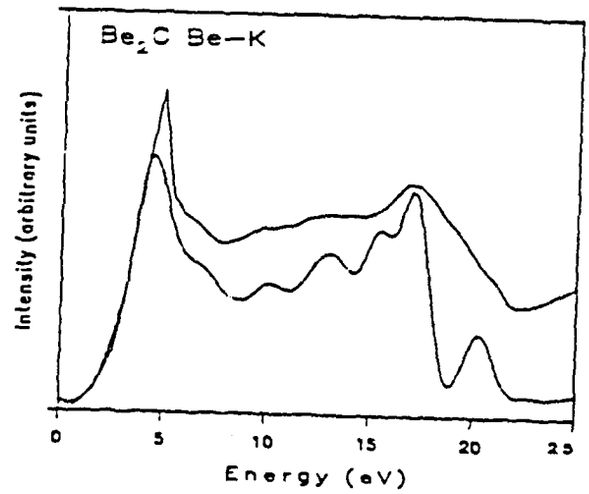
An addition area of work has been a collaboration with Professor K.T. Tsen, who does experimental work on time resolved pico-second spectroscopy. We have studied the expansion velocity of the photoexcited electron hole plasma in Si, and find it can be modeled with a hydrodynamic diffusion equation. We find a drift term due to the surface which depends strongly on lattice temperature [5].

Figure 8. (a) Band Structure of $Be_2C$. (b) Comparison between Be K near edge structure of $Be_2C$ (solid line) and theory (dashed line).




(a)

(b)



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